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Comparative Analysis of Dioxins and Furans by Electron Impact, High Resolution Mass Spectrometry and by Electron Capture, Negative Ionization, Low Resolution Mass Spectrometry

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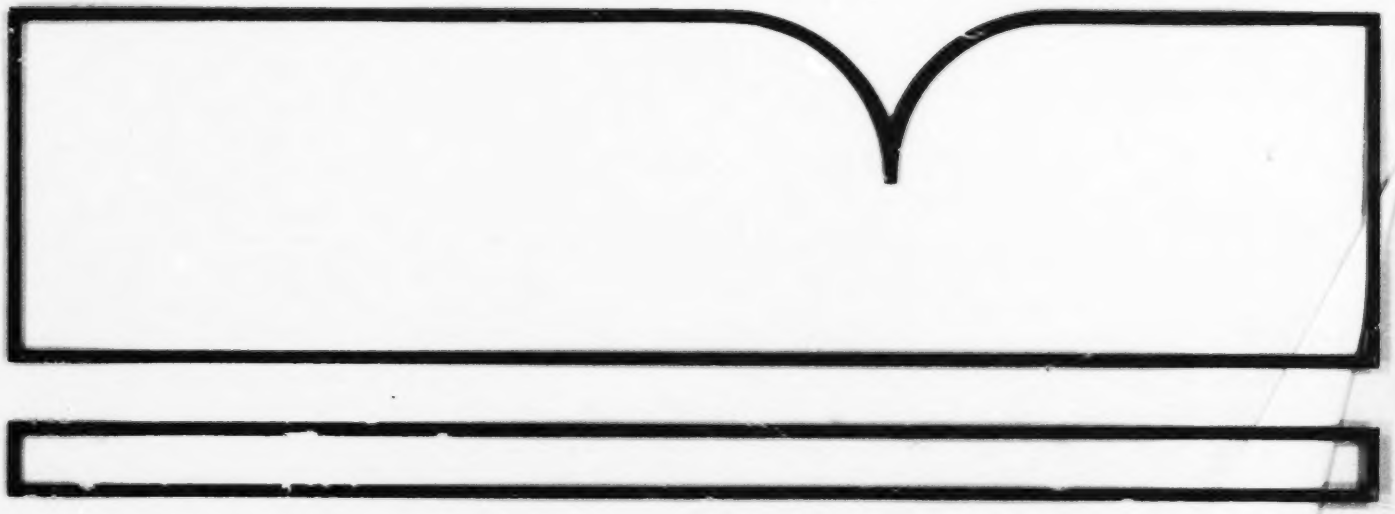

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16. ABSTRACT

→ Electron impact, high resolution mass spectrometry (HRMS) is currently the method of choice for the analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) because of its ability to detect PCDD/F in the presence of interfering compounds, such as PCB, which cannot be resolved by low resolution methods. The PCDD/F analyses may also be performed using electron capture, negative ionization (ECNI) low resolution mass spectrometry, providing extensive sample preparation is done to remove interferences. Before ECNI, low resolution MS can be accepted as a routine method for PCDD/F analysis, it is necessary to show that results generated by this method are comparable to those obtained by HRMS> Therefore, we have analyzed known mixtures and unknown air samples by electron impact HRMS (Finnigan MAT 90 system) and by ECNI, low resolution MS (Hewlett Packard 5985B). Both instruments were fitted with a gas chromatographic inlet. The PCDD/F concentrations determined by the two techniques compare favorably, typically within 20%. The major difference between these two methods is that the ECNI, low resolution method shows poor sensitivity in detecting 2, 3,7,8-tetrachlorodioxin. However, ECNI MS offers the advantage of lower detection limits (50-100 fg) than electron impact HRMS (0.1 to 0.5 pg). These results suggest that ECNI, low resolution MS can be a simple, low cost alternative to the common high resolution methods used for PCDD/F analysis.

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COMPARATIVE ANALYSIS OF DIOXINS AND FURANS BY ELECTRON IMPACT, HIGH RESOLUTION MASS SPECTROMETRY AND BY ELECTRON CAPTURE, NEGATIVE IONIZATION, LOW RESOLUTION MASS SPECTROMETRY

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Introduction. Electron impact high resolution mass spectrometry (HRMS) is currently the method of choice for the analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) because of its ability to detect PCDD/F in the presence of interfering compounds, such as polychlorinated biphenyls, which cannot be resolved by low resolution methods. PCDD/F analyses may also be performed using electron capture negative ionization (ECNI) low resolution mass spectrometry, if the sample is treated to remove interferences. ECNI low resolution MS is a useful technique because it offers sensitive detection for compounds with high electron affinities. ECNI detection limits for PCDD/F are 50-100 fg, while electron impact HRMS detection limits are 100-200 fg. In addition, the cost of an ECNI low resolution MS instrument is less than that of a HRMS instrument. Before ECNI can be accepted as a routine method for PCDD/F analysis, it is necessary to show that results generated by this method are comparable to those obtained by HRMS. Therefore, we have analyzed known mixtures and unknown air samples by electron impact HRMS and by ECNI low resolution MS, and we have compared the results of these analyses.

Experimental. *Samples:* Twelve air extracts were analyzed by both electron impact HRMS and by ECNI low resolution MS. Six samples were collected at Indiana University and spiked with $^{13}C_{12}$-1,2,3,7,8-pentachlorodibenzofuran (PCDF) and $^{13}C_{12}$-octachlorodibenzo-*p*-dioxin (OCDD). Interferents were removed by both silica and alumina column chromatography (*1*). Five samples were collected by the E.P.A. and prepared by their standard procedure (*2*, *3*). These samples were spiked with the following $^{13}C_{12}$-labeled compounds: 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), 1,2,3,4-TCDD, 2,3,7,8-tetrachlorodibenzofuran (TCDF), 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (PCDD), 1,2,3,7,8-PCDF, 1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin (HxCDD), 1,2,3,4,7,8-hexachlorodibenzofuran (HxCDF), 1,2,3,4,6.7,8-heptachlorodibenzo-*p*-dioxin (HpCDD), and OCDD. A PCDD/F standard provided by the E.P.A. was also analyzed.

I.U. Method: ECNI low resolution MS was performed at Indiana University using a Hewlett Packard 5985B mass spectrometer coupled with a Hewlett Packard 5840 gas chromatograph. Methane, at a pressure of 0.43 torr in the ionization source, served as the reagent gas. The temperature of the ionization source was 150°C. The samples were introduced into the MS through a 30 m x 0.25 mm DB-5 column. PCDD/F were detected using selected ion monitoring. The following ions served as quantitation and confirmation ions, respectively, for each congener class: 305.9 and 303.9 for TCDF, 321.9 and 319.9 for TCDD, 339.8 and 341.8 for PCDF, 351.8 for $^{13}C_{12}$-PCDF, 355.8 and 357.8 for PCDD, 373.8 and 375.8 for HxCDF, 389.8 and 391.8 for HxCDD, 388.7 and 390.7 for HpCDD, 407.7 and 409.7 for HpCDF, 422.7 for OCDD, 434.7 for $^{13}C_{12}$-OCDD, and 443.7 for OCDF. In addition to monitoring these ions, ions at 0.1 amu and 0.2 amu above and below the quantitation ion and ions at 0.1 amu above and below the confirmation ions were monitored. Quantitation was based on comparison of the combined peak areas of the 5 monitored ions to the peak area detected for a known amount of internal standard, considering the response factors, which were calculated daily. $^{13}C_{12}$-PCDF was used as an internal standard to quantitate the tetra-, penta-, and hexa-chlorinated dioxins and furans. $^{13}C_{12}$-OCDD was the internal standard used to quantitate the hepta- and octa-chlorinated dioxins and furans.

E.P.A. Method: Electron impact HRMS was done on a Finnigan MAT 90 system coupled with a Varian 3400 GC. The samples were introduced into the ionization source (held at 280°C) through a 30 m x 0.25 mm ID SE-54 column. The following quantitation and confirmation ions were monitored: 305.8987 and 303.9016 for TCDF, 317.9390 for $^{13}C_{12}$-TCDF, 321.8936 and 319.8965 for TCDD, 327.8847 for $^{37}Cl_4$-TCDD, 333.9338 for $^{13}C_{12}$-TCDD, 339.8597 and 341.8567 for PCDF, 351.8999 for $^{13}C_{12}$-PCDF, 355.8546

and 357.8517 PCDD, 367.8949 for $^{13}C_{12}$-PCDD, 373.8207 and 375.8178 for HxCDF, 385.8610 for $^{13}C_{12}$-HxCDF, 389.8156 and 391.8127 for HxCDD, 401.8559 for $^{13}C_{12}$-HxCDD, 407.7817 and 409.7788 for HpCDF, 423.7766 and 425.7737 for HpCDD, 435.8169 for $^{13}C_{12}$-HpCDD, 441.7428 and 443.7398 for OCDF, 457.7377 and 459.7347 for OCDD, and 471.7750 for $^{13}C_{12}$-OCDD. Quantitation of each congener class was accomplished by comparison to the area of the $^{13}C_{12}$-labeled standard of the same level of chlorination. An exception to this quantitation procedure was the analysis of the 6 samples provided by I.U.; in these cases, only $^{13}C_{12}$-PCDF and $^{13}C_{12}$-OCDD internal standards were used.

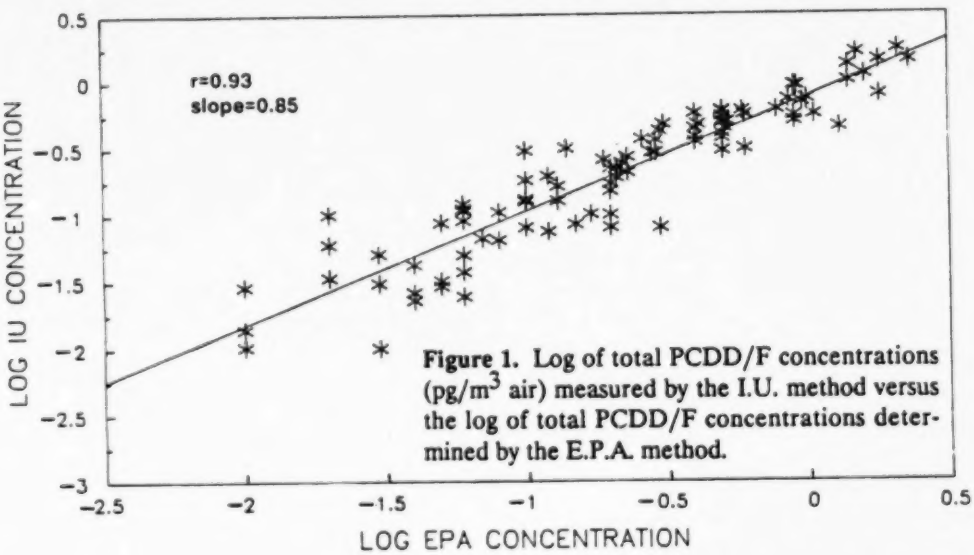

Figure 1. Log of total PCDD/F concentrations (pg/m^3 air) measured by the I.U. method versus the log of total PCDD/F concentrations determined by the E.P.A. method.

Results and Discussion. Despite the different methods of analysis, PCDD/F concentrations determined by ECNI, low resolution MS and electron impact HRMS are in good agreement; see Figure 1. PCDD/F levels based only on the concentrations of $^{13}C_{12}$-labeled PCDF and OCDD internal standards (I.U. method) were comparable to PCDD/F concentrations determined using a suite of ten $^{13}C_{12}$-labeled standards (E.P.A. method). Some minor differences between the two methods of analysis were noted. The concentrations of TCDF reported by I.U. are consistently lower than those reported by E.P.A., on average by a factor of 1.6. The major difference between the two methods is the detection of 2,3,7,8-TCDD, which is much less responsive than other TCDD isomers when using ECNI. This, in part, is attributed to extensive fragmentation of the 2,3,7,8-TCDD in the ECNI source. The chloride ion is the major fragment ion produced; ether cleavage ions are also observed. Other TCDD isomers, for example 1,2,3,4-TCDD, show little fragmentation. With electron impact ionization, all TCDD isomers exhibit similar mass spectral reponses. It should be noted that the lack of sensitivity in detecting 2,3,7,8-TCDD does not hinder the use of ECNI low resolution MS for the analysis of environmental samples because 2,3,7,8-TCDD is typically only a minor component. Overall, results generated by the two instrumental techniques agree well and suggest that ECNI low resolution MS can be a simple, low cost alternative to electron impact HRMS for PCDD/F analysis.

Literature Cited. 1. J. M. Czuczwa and R. A. Hites, *Environ. Sci. Technol. 18*, 444-450 (1984). 2. E.P.A. Method 600-3-85-019 (1986). 3. Proceedings of the 1988 E.P.A./A.P.C.A. International Symposium, 613-620. **Disclaimer.** This article has not been subjected to E.P.A. policy review; therefore, it does not necessarily reflect the views of the Agency and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. This research was funded by the U.S. Environmental Protection Agency through Grant Number CR 812588.